



# Integrated assessment of the impact of enhanced-efficiency nitrogen fertilizer on N<sub>2</sub>O emission and crop yield



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## ABSTRACT

Enhanced-efficiency nitrogen fertilizer (EENF) has gained considerable attention for improving nitrogen use efficiency and mitigating N<sub>2</sub>O emission in many agro-ecosystems. However, the effectiveness of EENF is highly variable under field condition. The factors influencing the efficacy of EENF are not well understood. Here, a meta-analysis was conducted to investigate the key factors affecting the efficacy of EENF in upland cropping systems. The effects of EENF were found to be similar among maize, wheat, and barley, while they varied among different EENF products. Inhibitors (IS), including nitrification inhibitors (NI), urease inhibitors (UI), and the combination of UI and NI, significantly mitigated N<sub>2</sub>O emission and increased crop yield, resulting in a greater reduction in yield-scaled N<sub>2</sub>O emission compared with slow- or control-releasing fertilizer (S/CRF). Reductions in yield-scaled N<sub>2</sub>O emission response to IS and S/CRF were both greater in arid regions than in humid regions. Soil pH and texture had less impact on the effect of IS than S/CRF. The efficacy of IS and S/CRF were not significant when N use rates were between 120 and 180 kg N ha<sup>-1</sup>. Surface broadcasting were unfavorable for mitigating N<sub>2</sub>O emissions with both IS and S/CRF. The impact of tillage on the efficacy of IS and S/CRF was affected by climate. The effectiveness of S/CRF depended more on these factors than did IS. This meta-analysis highlighted the necessity to connect EENF products with specific climatic, soil, and agronomic attributes for predicting their effectiveness.

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## 1. Introduction

Synthetic nitrogen (N) fertilizer has played a key role in enhancing crop production to feed 40% of the world's population since the Haber-Bosch process was invented in the 20th century (Crews and Peoples, 2004). Over the next 40 years, global N fertilizer for crop production is estimated to increase 1.4 fold to meet the projected food demand for 9 billion populations in 2050 (Tilman et al., 2001; Faostat, 2014). However, the increasing use of N fertilizer in crop production has been identified as a main contributor to the rising levels of atmospheric N<sub>2</sub>O, which is a long-lasting greenhouse gas that significantly contributes to

stratospheric ozone depletion and global climate change (Ravishankara et al., 2009). N<sub>2</sub>O emission is positively correlated with N application rates in linear or nonlinear relationships in agro-ecosystems (Shcherbak et al., 2014). Consequently, any further increase in N fertilizer application to ensure food security might further stimulate N<sub>2</sub>O emissions (Popp et al., 2010; Van Beek et al., 2010). Therefore, it is essential to mitigate N<sub>2</sub>O emission by improving N use efficiency (NUE).

Enhanced-efficiency nitrogen fertilizer (EENF) is designed to reduce potential N loss to the environment and to improve N use efficiency (Halvorson et al., 2014). The main EENF products are slow- or control-releasing fertilizer (S/CRF) and normal N sources treated with nitrification inhibitors (NI) and/or urease inhibitors (UI; Dell et al., 2014). Many reviews (Smith et al., 1997; Oenema et al., 2001; Akiyama et al., 2010; Decock, 2014; Halvorson et al., 2014) and IPCC reports (Smith et al., 2007, 2014) have suggested these products as mitigation options for N<sub>2</sub>O emission from cropland soils. However, increasing evidence from field experiments showed that the performances of EENF were highly variable

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across studies. Some studies reported that EENF significantly mitigated N<sub>2</sub>O emissions compared with normal N fertilizer (Halvorson et al., 2010), and others no significant difference (Chu et al., 2007), or even significantly higher N<sub>2</sub>O emissions (Hu et al., 2013) with EENF. Furthermore, EENF affects both N<sub>2</sub>O emission and crop yield. The integrated effect of EENF on N<sub>2</sub>O emission and crop yield is still uncertain. Reduced N<sub>2</sub>O emission with either significantly increased (Ma et al., 2013), decreased (Asgedom et al., 2014), or unchanged (Halvorson and Del Grosso, 2013) crop yield has been observed in previous studies. These contradictory results indicate the highly complex nature of the effect of EENF on N<sub>2</sub>O emission and crop yield.

The mechanisms underlying the effects of EENF on N<sub>2</sub>O emission are mainly through limiting the substrate pools available for the microbial process of N<sub>2</sub>O production (Malla et al., 2005; Halvorson et al., 2014). For example, S/CRF can reduce the rate of N release to better match crop uptake; while NI delays the oxidation of ammonia (NH<sub>4</sub><sup>+</sup>) to nitrite (NO<sub>2</sub><sup>-</sup>) and then nitrate (NO<sub>3</sub><sup>-</sup>); and UI prevents the transformation of urea to NH<sub>4</sub><sup>+</sup> (Trenkel, 2010). However, these effects on subsurface processes might be affected by climate, soil properties, or agronomical practices. Soil pH might affect the retention time and the effect of NI (Hendrickson and Keeney, 1979; Xue et al., 2012). Meanwhile, agronomical practices might indirectly affect nutrient release from EENF by changing soil properties. For instance, compared with conventional tillage, no-tillage can increase soil bulk density and moisture (De Vita et al., 2007), which in turn may weaken the effect of S/CRF on delay N release from fertilizer. Furthermore, management practices also directly affect N source competition of N<sub>2</sub>O production and plant uptake by adjusting fertilizer application rates and timings (Drury et al., 2012). Therefore, a better understanding of the impacts of these factors on the effects of EENF will provide good guidelines for

the application of EENF in order to mitigate N<sub>2</sub>O emission with increased crop yield.

Considering the balance of food security and greenhouse gas mitigation, increasing numbers of studies have proposed that an integrated assessment of yield-scaled N<sub>2</sub>O emission will be particularly important for these practices such as EENF affected both N<sub>2</sub>O emission and crop yield (Van Groenigen et al., 2010; Linquist et al., 2012; Van Kessel et al., 2013). Many previous studies focused mainly on assessing the effects of EENF on either crop yield or area-scaled N<sub>2</sub>O emission (Chen et al., 2008; Akiyama et al., 2010; Linquist et al., 2013; Abalos et al., 2014; Qiao et al., 2015; Gilsanz et al., 2016; Yang et al., 2016). The integrated effects of EENF on yield-scaled N<sub>2</sub>O emission and the corresponding key influencing factors are still unclear. Therefore, a meta-analysis based on peer-reviewed studies was conducted to (i) evaluate the effects of EENF on N<sub>2</sub>O emissions and agronomic performance, compared with conventional nitrogen fertilizer; (ii) evaluate the impacts of climate (aridity), soil properties (soil pH and texture), fertilizer application strategies (application rate, timing and placement), and soil tillage on the efficacy of EENF.

## 2. Materials and methods

### 2.1. Data collection

A literature survey of peer-reviewed papers published before March 2015 reporting the results of the effects of EENF on N<sub>2</sub>O emission was carried out using the ISI-Web of Science and Google Scholar. The literature survey mainly focused on N<sub>2</sub>O emission from upland cropping systems including maize, wheat, and barley; horticulture crops were excluded. Only studies that met the following criteria were included: (i) the measurements were

**Table 1**

The studies used in the meta-analysis to evaluate the impacts of EENF on N<sub>2</sub>O emission and crop yield.

Id	Crop	Country	Number of comparisons	Type of EENF	Reference	Id	Crop	Country	Number of comparisons	Type of EENF	Reference
1	Wheat	India	4	NI	Majumdar et al., 2002	21	Maize	USA	4	S/CRF, UI +NI	Venterea et al., 2011
2	Wheat	India	6	UI, NI	Malla et al., 2005	22	Maize	Canada	18	S/CRF	Drury et al., 2012
3	Wheat	India	2	NI	Pathak et al., 2002	23	Maize	China	2	S/CRF, NI	Yang et al., 2014
4	Wheat	China	4	NI	Ma et al., 2013	24	Maize	USA	6	NI	Burzaco et al., 2013
5	Wheat	India	6	NI	Bhatia et al., 2010	25	Maize	USA	1	S/CRF	Nash et al., 2012
6	Wheat	China	5	S/CRF	Ji et al., 2012	26	Maize	USA	14	S/CRF, UI +NI	Dell et al., 2014
7	Wheat	China	2	NI, S/CRF	Hu et al., 2014	27	Maize	USA	6	S/CRF, UI +NI	Halvorson & Del Grosso, 2013
8	Wheat	China	2	S/CRF	Zhang et al., 2014	28	Maize	USA	2	UI, S/CRF	Maharjan et al., 2014
9	Barley	Japan	1	S/CRF	Chu et al., 2007	29	Maize	USA	6	S/CRF, UI +NI	Sistani et al., 2011
10	Barley	USA	2	NI, S/CRF	Delgado & Mosier, 1996	30	Maize	China	3	S/CRF	Liu et al., 2013b
11	Maize	China	3	S/CRF	Shi, 2012	31	Barley	Spain	1	UI	Abalos et al., 2012
12	Maize	China	2	NI, S/CRF	Liu, 2011	32	Wheat	Canada	2	UI+NI, S/CRF	Asgedom et al., 2014
13	Maize	China	2	NI, UI+NI	Huang et al., 1998	33	Maize	USA	5	S/CRF, UI +NI	Maharjan & Venterea, 2013
14	Maize	China	3	NI, UI, NI +UI	Ding et al., 2011	34	Wheat, Maize	China	8	S/CRF, NI	Hu et al., 2013
15	Maize	USA	8	S/CRF, UI +NI	Halvorson et al., 2010	35	Wheat, Maize	China	4	NI	Liu et al., 2013a
16	Maize	USA	2	NI	Parkin & Hatfield, 2010	36	Wheat, Maize	Australia	2	NI	Migliorati et al., 2014
17	Maize	Japan	1	S/CRF	Yan et al., 2001	37	Wheat, Maize	China	2	S/CRF	Shi et al., 2013
18	Maize	USA	6	S/CRF, UI +NI	Halvorson & Del Grosso, 2012	38	Wheat, Maize	Germany	4	NI	Weiske et al., 2001
19	Maize	USA	10	S/CRF, UI +NI	Halvorson et al., 2011	39	Wheat	Spain	4	NI	Huérffano et al., 2015
20	Maize	Spain	4	UI, UI+NI	Sanz-Cobena et al., 2012	40	Wheat	Canada	8	S/CRF, UI +NI	Gao et al., 2015

conducted under field conditions; (ii)  $\text{N}_2\text{O}$  flux rate must have been measured for an entire crop growth period; (iii) the nitrogen source and application rate were same for the treatment and control; and (iv) the grain yields were reported. According to these criteria, forty papers including 177 comparisons (Table 1) were selected for this analysis. The detailed database is listed in Supplementary Table A1. The distribution of experimental sites is shown in Supplementary Fig. A1.

In this analysis, EENF were classified as inhibitors (IS, including NI, UI and UI + NI) or S/CRF according to their mode of action. And their individual effects on  $\text{N}_2\text{O}$  emission and NUE were examined. In selected studies, the most tested NI products were Dicyandiamide (DCD), 3,4-Dimethylpyrazole phosphate (DMPP), and Nitrapyrin. Other nitrification inhibitors, such as neem oil, neem cake, and S-benzylisothiuronium butanoate, were examined in only one or two studies. The main UI and S/CRF products were *N*-(*n*-butyl) phosphoric triamide (NBPT) and polymer-coated fertilizer (PCF), respectively.

To evaluate the effects of climate, soil properties, and agronomic practices, subgroups of studies were classified according to climate aridity, soil pH, texture, N application rate, timing and placement, and soil tillage. Climate aridity index was determined following the generalized climate classification scheme for Global-Aridity values (Trabucco and Zomer, 2009). Aridity was classified as humid (aridity index > 0.65) and arid (aridity index ≤ 0.65). Soil pH was categorized into three groups: < 6.5, 6.5–7.5, and > 7.5. Soil texture was grouped into three categories: fine (clay, silt clay, sandy clay), medium (clay loam, loam, silt clay loam, silt, silt loam) and coarse (sandy loam, sandy clay loam, loamy sand; USDA, 1999). The rates of N application were empirically divided into three levels (≤ 120, 120–180, and ≥ 180 kg N ha<sup>-1</sup> season<sup>-1</sup>). N application timing was categorized into three groups: applied before emergence as a basal fertilizer (Basal); applied after emergence as a top dressing fertilizer (Top dressing); split applied as both basal and top dressing fertilizer (Split). N placement was categorized according to horizontal (broadcast and band) and vertical distribution (surface and incorporated): surface broadcast (SBC), broadcast incorporated (BCI), surface band (SB), band incorporation (BI). Finally, for soil tillage practices, three groups of no-tillage (NT), reduced tillage (RT), and conventional tillage (CT) were analyzed.

## 2.2. Data analysis

The impacts of EENF on area- and yield-scaled  $\text{N}_2\text{O}$  emissions, crop yield, and NUE were evaluated by the response ratio (R; Hedges et al., 1999).

$$\ln R = \ln(x_t/x_c) \quad (1)$$

where  $x_t$  and  $x_c$  are the measurements for EENF and conventional inorganic N fertilizer, respectively. NUE was only calculated for the studies with no N treatment. The number of NUE comparisons (121) was less than that of  $\text{N}_2\text{O}$  emission and yield (177).

Furthermore, the mean of the response ratios was calculated from  $\ln R$  of individual studies by

$$M = \text{EXP}\left(\sum [\ln R(i) \times w(i)] / \sum w(i)\right) \quad (2)$$

In Formula (2),  $w(i)$  is the weighting factor and is estimated by

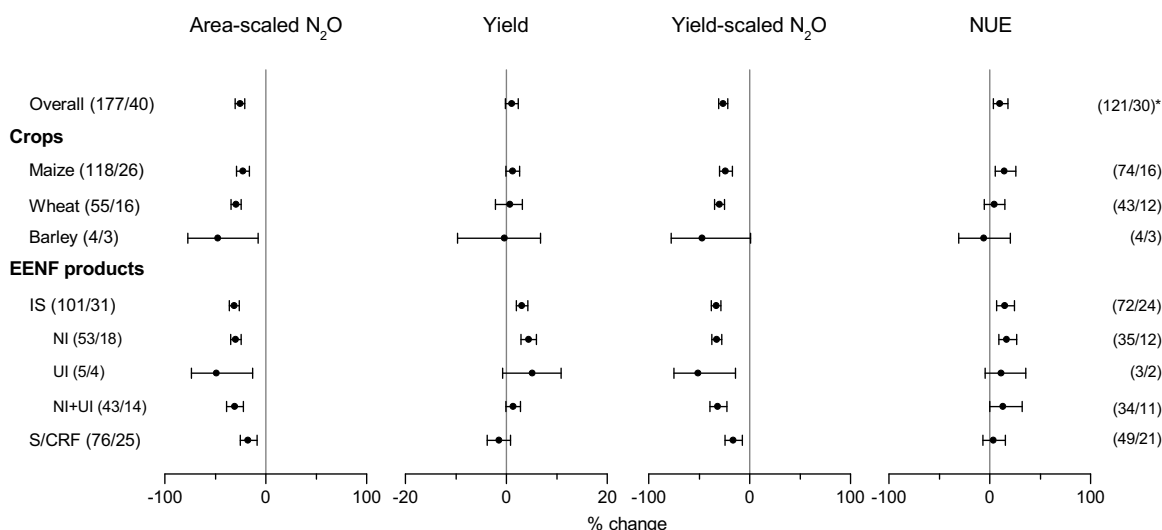
$$w(i) = n \times f \quad (3)$$

where  $n$  is the number of experiment replicates; and  $f$  is the number of  $\text{N}_2\text{O}$  flux measurements per month. This weighting approach assigns more weight to field experiments that were well replicated. The meta-analysis was performed using the MetaWin 2.1 (Rosenberg et al., 2000). Mean effect sizes were estimated with a Random-effects model. The 95% confidence intervals (CIs) around mean effect sizes were calculated by using bootstrapping with 4999 iterations (Rosenberg et al., 2000; Linquist et al., 2012).

## 3. Results and discussion

### 3.1. Difference among crops and EENF products

On average, EENF significantly reduced area- and yield-scaled  $\text{N}_2\text{O}$  emissions by 25.6% and 26.4%, respectively, compared with conventional N fertilizer. The NUE was significantly enhanced 10.2% by EENF (Fig. 1). No significant difference was found in the effects of EENF on  $\text{N}_2\text{O}$  emission and crop yield among the crops of maize, wheat, and barley. However, the effects varied significantly among different EENF products. The IS significantly mitigated area-scaled  $\text{N}_2\text{O}$  emission by 31.5% and increased yield by 3.1%, compared with conventional N fertilizer. Yield-scaled  $\text{N}_2\text{O}$  emission was reduced 33.2% by IS. The efficacy of NI on  $\text{N}_2\text{O}$



**Fig. 1.** Effects of EENF on area-scaled  $\text{N}_2\text{O}$  emission, crop yield, yield-scaled  $\text{N}_2\text{O}$  emission and NUE among different EENF products and crops. The numbers of comparisons and studies are indicated in the parentheses; \* the numbers of comparisons and studies for NUE, which is less than that for  $\text{N}_2\text{O}$  and crop yield, because 10 studies did not reported the result of no N treatment; all error bars represented 95% confidence intervals (Similarly hereinafter). The abbreviations in this figure were: IS: inhibitors; NI: nitrification inhibitors; UI: urease inhibitors; S/CRF: slow/controlled releasing fertilizer.

emission and crop yield was higher than the other inhibitors. The area- and yield-scaled  $\text{N}_2\text{O}$  emissions were significantly mitigated 29.7% and 32.6% by NI, respectively; and the crop yield and NUE were significantly increased 4.4% and 16.9% by NI, respectively. The UI also showed a negative effect on  $\text{N}_2\text{O}$  emission and a positive effect on crop yield, but its impact on crop yield was not significant due to a wide 95% CI. The combination of UI + NI did not perform better than NI alone. The mean effect sizes of UI + NI on  $\text{N}_2\text{O}$  emission and crop yield were similar to NI. As for S/CRF, area-scaled  $\text{N}_2\text{O}$  emission was significantly mitigated by 17.5%; however, its effects on crop yield and NUE were not significant. Yield-scaled  $\text{N}_2\text{O}$  emission was significantly reduced 16.3% by S/CRF, which was significantly lower than that of IS.

Compared with previous evaluations, the mean effect size of NI on  $\text{N}_2\text{O}$  emission was similar to the result reported by Akiyama et al. (2010); however, the effect size of S/CRF was not. Akiyama et al. (2010) reported that PCF (a main type of S/CRF) did not produce significant effect on  $\text{N}_2\text{O}$  emission in upland fields compared with normal N fertilizer; while a significant reduction (−16.0%) of  $\text{N}_2\text{O}$  emission to PCF was observed in this analysis (Appendix Fig. A2). Such a difference in the effect of PCF could be due to the more comprehensive dataset ( $n = 73$ ) as compared with fewer observations previously ( $n = 13$ ). Thus, we suggest that the result of this analysis is more reliable.

The results of UI and UI + NI on crop productivity in this analysis were inconsistent with that reported by Linquist et al. (2013) and Abalos et al. (2014). This was possibly attributed to the difference in crops between this analysis and other two studies. Linquist et al. (2013) mainly evaluated the effect of inhibitors on rice, and the results showed that UI, and UI + NI both produced a significant benefit on rice yield. However, in this analysis, the effects of UI and UI + NI on the yield of upland cereal crops (wheat, maize and barley) were not significant (Fig. 1). This was possibly due to the different climatic factors during rice and upland crops growing seasons. Ammonia volatilization was higher in the rice season than in the maize and wheat seasons due to higher temperature and solar radiation (Cai et al., 2002). Thus, UI and UI + NI were perhaps more effective in inhibiting N loss to the environment and thus benefited rice yield. Abalos et al. (2014) evaluated not only cereal crops but also forage crops (nearly half of the total comparisons). The N application rates were higher for forage crops than cereals, so the effect of inhibitors was more responsive on forage crops.

### 3.2. Impact of climate aridity

Climate aridity had a significant effect on the efficacy of IS and S/CRF on  $\text{N}_2\text{O}$  emission and NUE (Fig. 2). Both IS and S/CRF produced higher effects on the mitigation of  $\text{N}_2\text{O}$  emission in arid than in humid regions. The area- and yield-scaled  $\text{N}_2\text{O}$  emissions were, respectively, reduced by 37.4% and 39.9% as a result of IS application in arid regions; the reduction of  $\text{N}_2\text{O}$  emissions was significantly higher than that in humid regions. S/CRF significantly mitigated area- and yield-scaled  $\text{N}_2\text{O}$  emissions by 25.8% and 25.9% in arid regions, respectively; but did not show a significant effect on  $\text{N}_2\text{O}$  emissions in humid regions. In addition, both IS and S/CRF only showed significant positive effects on NUE in arid regions.

Climate aridity is an indicator of rainfall and potential evapotranspiration. Intensive precipitation may lead to the translocation of NI within soil, resulting in the spatial separation of NI from  $\text{NH}_4^+$  to be stabilized (Zerulla et al., 2001). Furthermore, high moisture may increase the leaching loss of IS (Puttanna et al., 1999). Though some studies have demonstrated that UI or NI were effective in mitigating  $\text{N}_2\text{O}$  emission at high soil moisture (Macadam et al., 2003; Burzaco et al., 2013), it has also been observed that UI and NI produced no effect on  $\text{N}_2\text{O}$  emission when water-filled pore space was >60% (Menéndez et al., 2009). Thus, a humid climate was unfavorable for IS to slow down the transformation of N. As for S/CRF, the process of N release from S/CRF usually consists of two steps: water penetrates into the granules and dissolves the fertilizer; then the fertilizer solution flows out through pores over a concentration gradient across the coating (Shaviv, 2001). High soil moisture increases N release from S/CRF, which weakens the effect of S/CRF on controlling N release.

We further analyzed the effective of IS and S/CRF under irrigated and rainfed conditions in arid regions (Fig. 2). The effects of IS didn't show significantly difference on  $\text{N}_2\text{O}$  emissions, crop yield and NUE under irrigated and rainfed conditions. Whereas, irrigation significantly enhanced the inhibition effect of S/CRF on  $\text{N}_2\text{O}$  emissions. The reduction of  $\text{N}_2\text{O}$  emissions response to S/CRF was significantly higher under irrigated than rainfed fields. Irrigation is usually carried out immediately after fertilization, which could increase the  $\text{NO}_3^-$  leaching loss and intensity the adequate of available N to  $\text{N}_2\text{O}$  production (Maharjan et al., 2014). Thus, the combination of irrigation and S/CRF reduced more  $\text{N}_2\text{O}$  emission. However, high  $\text{NO}_3^-$  leaching loss may decrease the uptake of N by crops. This was a possible reason to explain why S/

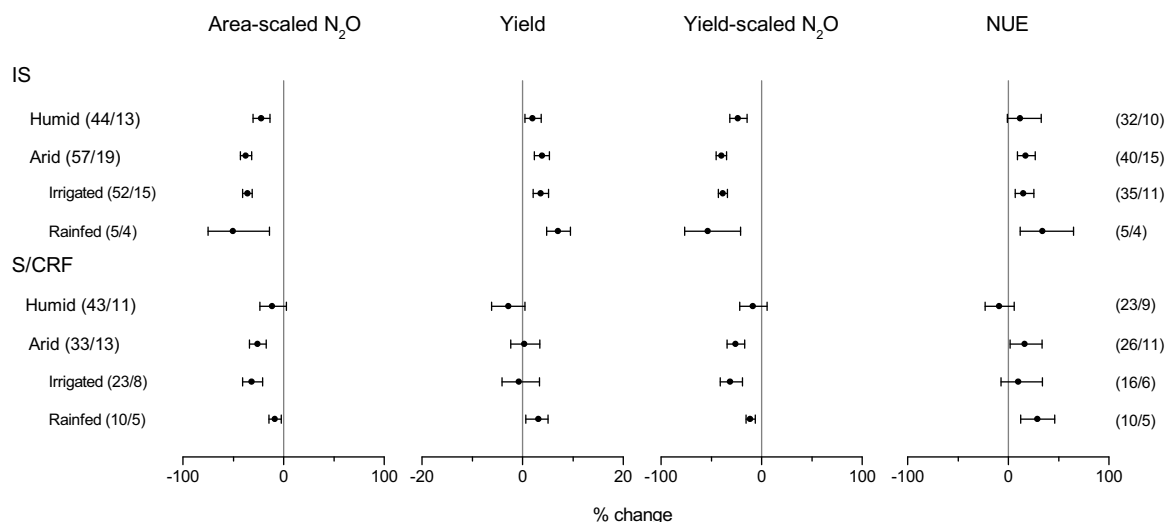


Fig. 2. Impacts of aridity on the effects of EENF on area- and yield-scaled  $\text{N}_2\text{O}$  emissions, crop yield and NUE.



CRF significantly enhanced NUE in rainfed fields, but didn't show significant effect on NUE in irrigated fields.

### 3.3. Impact of soil pH and texture

The effects of IS and S/CRF varied with soil pH value (Fig. 3). IS performed better in alkaline than neutral and acid soils. The increase in crop yield and NUE with IS was only significant in alkaline soil. This was consistent with the results reported by Yang et al. (2016), but different from the results reported by Abalos et al. (2014). The discrepancy between this study and Abalos et al. (2014) primarily attributed to the difference in crops. The IS tended to reduce more yield-scaled  $N_2O$  emission in alkaline (37.8%) than neutral (26.7%) and acid soils (27.4%); however, the difference was not significant. The higher efficiency of IS in alkaline soil was possibly because that NI was better retained and more susceptible to nitrifier population in high pH than low pH soils (Hendrickson and Keeney, 1979; Xue et al., 2012). The S/CRF only significantly mitigated the area- and yield-scaled  $N_2O$  emissions by 29.3% and 28.8% in alkaline soil, and by 35.0% and 34.6% in neutral soil, respectively. Its effect on  $N_2O$  emissions was not significantly in acid soil. Unlike IS, soil pH had little effect on nutrient release from S/CRF (Trenkel, 2010). The significantly reduction in  $N_2O$  emission in neutral and alkaline soils may attribute to that high soil pH promoted the  $NO_3^-$  loss or ammonia volatilization than low soil pH (Kyveryga et al., 2004), which intensified the adequacy of available N for nitrification and denitrification processes.

The area-scaled  $N_2O$  emission was significantly reduced 27.9% by IS in medium soil (Fig. 4), which consisted with the results reported by Gilsanz et al. (2016). The inhibitory effect of IS on area-scaled  $N_2O$  emission was not affected by soil texture. However, the effect of IS on crop yield and NUE depended on soil texture. Enhancement of crop yield and NUE with IS was significant in coarse and medium soils, but not in fine soil. This was consistent with the results of a previous study (Pasda et al., 2001). Crop yields response to NI was more pronounced in light textured soils; as the effects of NI were negatively correlated with clay content and positively correlated with soil sand content (Gioacchini et al., 2002; Barth et al., 2008).

As for S/CRF, its effects on  $N_2O$  emission and crop yield both depended on soil texture (Fig. 4). Area-scaled  $N_2O$  emission was significantly mitigated 18.2% and 43.9% by S/CRF in medium and fine soils, respectively, but not reduced by S/CRF in coarse soil. S/CRF showed no significant impact on crop yield in coarse and medium soils, but significantly reduced crop yield in fine soil. Yield-scaled  $N_2O$  emission was only mitigated 34.2% by S/CRF in fine soil due to the reduction in crop yield. The influence of soil

texture on the release of N from S/CRF has not been well documented. The results of laboratory incubation showed that N release from S/CRF was more rapidly in clayey than sandy soils due to the higher urease activity, which was positively correlated with clay content (Golden et al., 2011). While a field experiment proposed that higher cation exchange capacity in clay soil increased the adsorption of  $NH_4^+$  compared with sandy soil (Jarecki et al., 2008), which perhaps inhibited the release of N from S/CRF. The results of this analysis were consistent with the latter; that soil clay content benefits the delay of N release from S/CRF. Thus S/CRF significantly reduced  $N_2O$  emission in medium and fine soils, but not in coarse soil (Fig. 4). This also explained why S/CRF significantly reduced crop yield in fine soil.

### 3.4. Impact of N application rate, timing, and placement

Application rates, timing, and placement of N fertilizer were the primary management practices determining N use efficiency and N loss to the environment. We separately analyzed the effect of EENF on wheat and maize under different N application rates in order to avoid the bias among crops (Fig. 5). The results showed that IS and S/CRF both significantly reduced the  $N_2O$  emission from wheat field under low ( $\leq 120 \text{ kg N ha}^{-1}$ ) or high N rates ( $\geq 180 \text{ kg N ha}^{-1}$ ). The effectiveness of IS and S/CRF on  $N_2O$  emission were similar under different N rates during wheat season. Interestingly, both IS and S/CRF significantly mitigated the  $N_2O$  emission at low and high N rates, but not at medium N rates ( $120\text{--}180 \text{ kg N ha}^{-1}$ ) during maize season. This was inconsistent with previous study (Yang et al., 2016). The response of  $N_2O$  emission to N use rates was primarily regulated by the competition between crop uptake and soil microbe for available N (Kim et al., 2013). Soil microbes were the strongest competitors for fertilizer N in short term (up to several days), but crop outcompete soil microbes in long term (weeks to months) (Inselsbacher et al., 2010). We speculated that, at low N application rate, maize uptake possibly might outcompete the microbial process of  $N_2O$  production due to the limited N source. Thus, the inhibition or delay of N release from fertilizer by EENF perhaps benefit the crop uptake and inhibit  $N_2O$  production. With the N rates increased to medium amount, the N competition of maize and soil microbe might be less severe. The effects of EENF on  $N_2O$  emission and maize yield were depended on whether the inhibited or delayed N matched crop demand. If the inhibited N was not absorbed by crop plants, EENF may benefit the microbial process of  $N_2O$  production and raise  $N_2O$  emission. Therefore, either reduced or increased  $N_2O$  emissions with EENF at medium N rate were observed (Nash et al., 2012; Asgedom et al., 2014; Dell et al., 2014). And its integrated effect was not significant on  $N_2O$

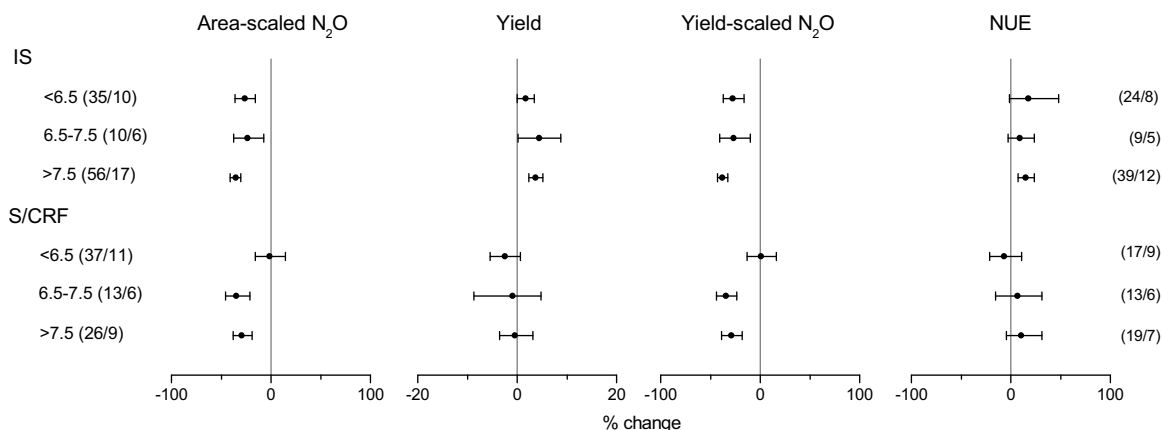


Fig. 3. Impacts of soil pH on the effects of EENF on area- and yield-scaled  $N_2O$  emissions, crop yield and NUE.

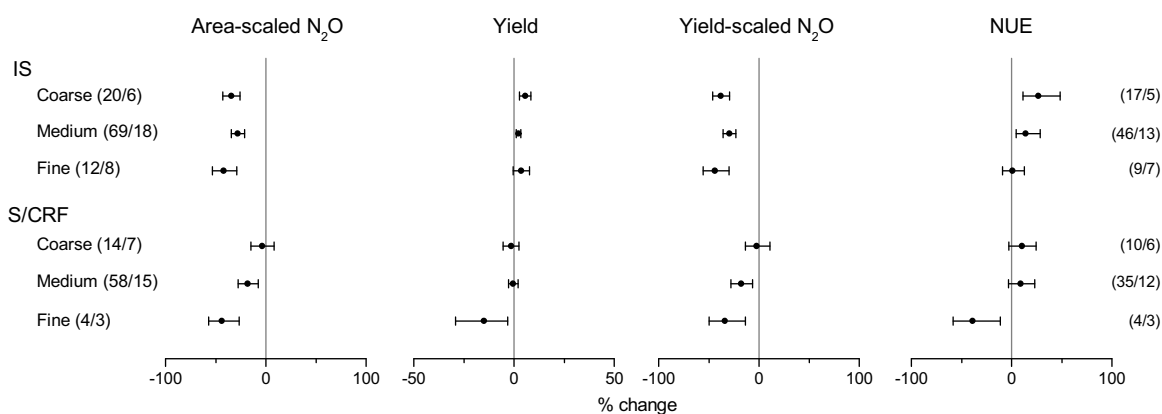


Fig. 4. Impacts of soil texture on the effects of EENF on area- and yield-scaled N<sub>2</sub>O emissions, crop yield and NUE.

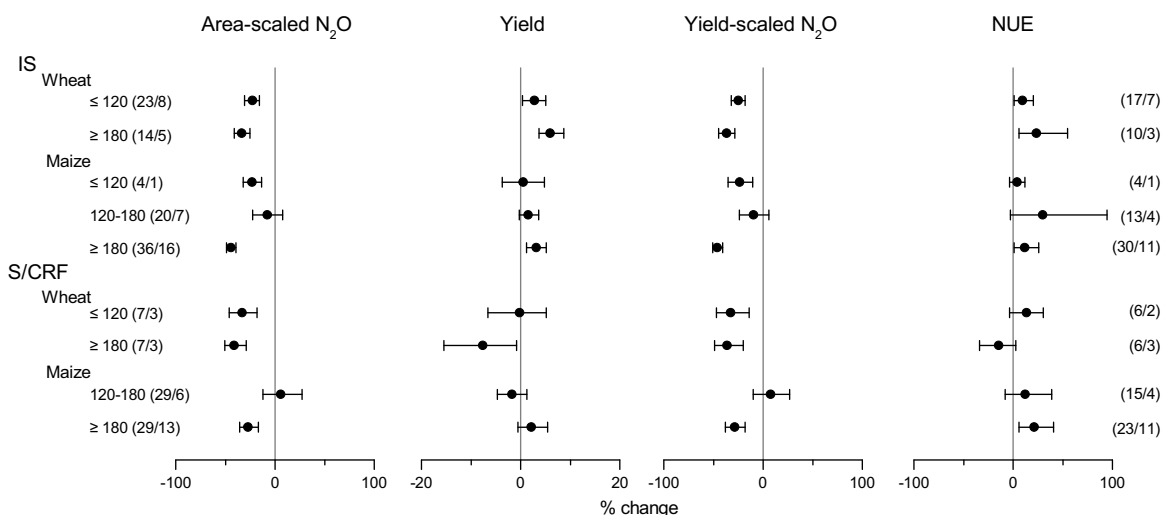


Fig. 5. Impacts of N application rates on the effects of EENF on area- and yield-scaled N<sub>2</sub>O emissions, crop yield and NUE.

emission and crop yield. While at high N application rates, the N was enough for maize demand; the primary factor control the N<sub>2</sub>O emission was the residual N available for the microbial process of nitrification and denitrification (Kim et al., 2013). Thus, the inhibition or delay of N release from fertilizer by EENF inhibited the N<sub>2</sub>O emission.

The application timing of N fertilizer is a practice that adjusts the synchrony between N supply and N demand. The results of this analysis showed that the mean effectiveness of IS was not affected by application timing; IS significantly mitigated yield-scaled N<sub>2</sub>O emissions under all three application timings (Fig. 6). While the effects of S/CRF varied with fertilizer application timing, S/CRF only

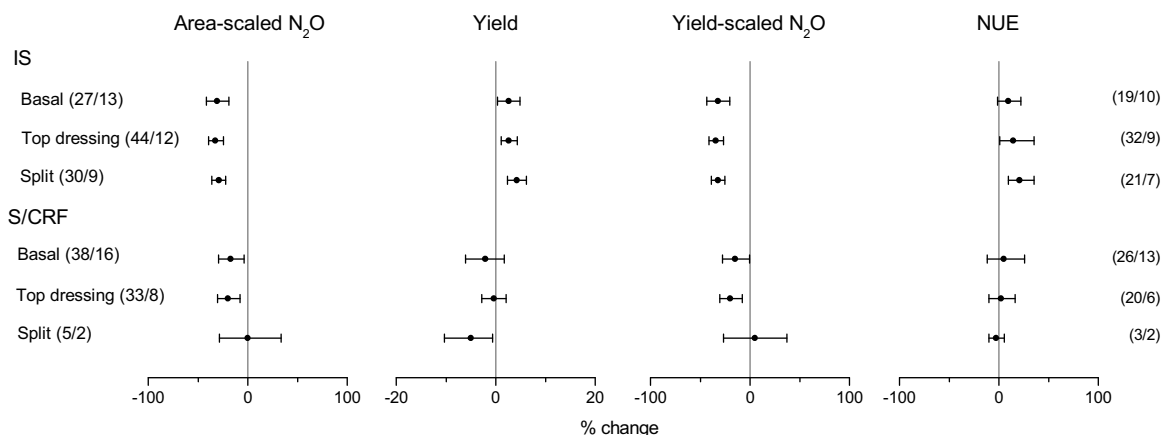


Fig. 6. Impact of fertilizer application timing on the effects of EENF on area- and yield-scaled N<sub>2</sub>O emissions, crop yield and NUE.

showed significant effects on area- and yield-scaled  $N_2O$  emissions when N was applied after emergence as a top dressing fertilizer. The area- and yield-scaled  $N_2O$  emissions were reduced by 20.0% and 19.8%, respectively. This was possibly because the effectiveness of S/CRF depended more on the synchrony between N supply and crop uptake than that of IS. Applying N fertilizer after plant emergence (e.g. at the six-leaf stage of maize) could better match crop demand, increase N uptake by plants, and reduce N loss to the environment (Rozas et al., 2004). However, when S/CRF was split applied, S/CRF showed no significant effect on area-scaled  $N_2O$  emission and significant negative effect on crop yield. This was possibly attributed to application method of top dressing N fertilizer. In this subgroup, the top dressing N fertilizer was mostly surface applied with flood irrigation, which may increase the N loss and limit the effect of S/CRF. While in the subgroup of “Top dressing”, the N fertilizer was applied with sprinkler irrigation or without irrigation. It should be noted that the results in Fig. 2 showed that irrigation benefited the S/CRF to mitigate  $N_2O$  emission. It was possibly because that the impact of irrigation on efficacy of S/CRF depended on irrigation methods. S/CRF significantly mitigated the  $N_2O$  emission in sprinkler irrigation field, but did not in flood irrigation field (Fig. A3).

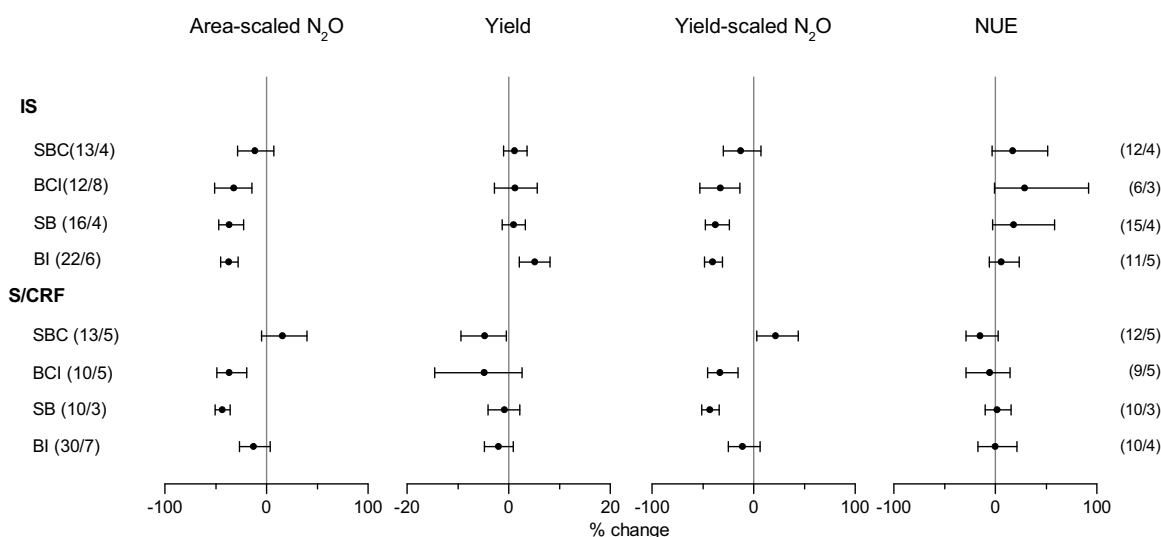
The effects of IS and S/CRF were also influenced by placement methods (Fig. 7). The SBC was not conducive to IS and S/CRF to adjust the release and transformation of N. The IS did not produce a significant effect on  $N_2O$  emissions and crop yield, and S/CRF even significantly raised yield-scaled  $N_2O$  emission when applied by SBC. The SBC spreads the fertilizer uniformly over the soil surface causing greater soil contact with fertilizer granules (Nash et al., 2012), which potentially increases the degradation of IS due to the greater contact with soil microbes and higher temperature at the soil surface (Irigoyen et al., 2003). As for S/CRF, higher temperature and wider contact with soil microbes resulted in higher rates of several N transformation processes (e.g. ammonia volatilization, nitrification and denitrification) (Nash et al., 2012), which would increase N release and weaken the efficacy of S/CRF. However, S/CRF significantly reduced  $N_2O$  emission under SB, but not under BI (Fig. 7). The difference between SB and BI is perhaps primarily attributed to their impact on soil moisture. Halvorson and Del Grosso (2012) have reported that BI usually kept fertilizer granules

wetter longer than SB, thus increasing N release from S/CRF. Field studies (Sistani et al., 2011; Maharjan and Venterea, 2013) also observed that BI S/CRF only significantly mitigated  $N_2O$  emission during drier years, but not during wetter years.

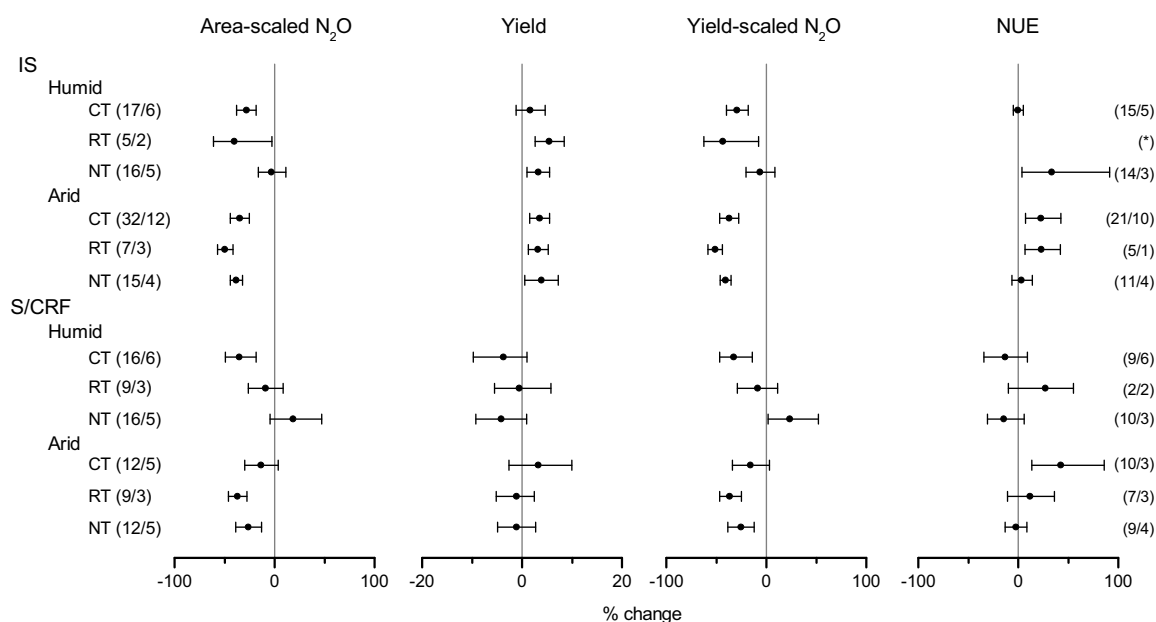
### 3.5. Impact of soil tillage

The effectiveness of IS was not affected by the tillage methods in arid areas. IS significantly mitigated the area- and yield-scaled  $N_2O$  emissions and increased crop yield under all three tillage methods in arid areas (Fig. 8). However, as in humid regions, IS did not significantly mitigate the  $N_2O$  emission under NT method. This can be explained by two possible reasons. Firstly, NT generally tends to increase soil moisture and bulk density compared with CT, resulting in greater water-filled pore space (Venterea et al., 2011), which tends to weaken the inhibitory effect of IS on urease and nitrification processes. Secondly, a potential interaction of tillage with placement methods affected the efficacy of IS (Nash et al., 2012). Nearly 41% of the observations in the NT group were surface broadcast, which was not conducive to the effects of IS on  $N_2O$  emission.

The impact of tillage on the effectiveness of S/CRF was opposite in humid and arid areas (Fig. 8). The S/CRF significantly mitigated the  $N_2O$  emission under CT, but did not under RT and NT in humid areas, indicating that CT benefited S/CRF to reduce  $N_2O$  emission in humid areas. While in arid regions, it was opposite. It was possible that the dominant impact of soil tillage on the effectiveness of S/CRF was different in humid and arid areas. As in humid regions, greater water-filled pore space and anaerobic condition caused by frequent precipitation may be the key factor influencing the effect of S/CRF. As compared with NT and RT, CT tended to increase the soil porosity and to decrease the soil moisture and anaerobic condition (Mangalassery et al., 2014), which may promote the mitigation of S/CRF on  $N_2O$  emission. While in arid areas, the activity of microbial process related to nitrification and denitrification may be the primary factor affecting the effect of S/CRF. The CT could turn the crop residue into subsurface soil and increased the microbial biomass carbon, which may enhance the potential of  $N_2O$  production and weaken the effectiveness of S/CRF.



**Fig. 7.** Impact of fertilizer placement methods on the effects of EENF on area- and yield-scaled  $N_2O$  emissions, crop yield and NUE. The abbreviations in this figure were: SBC: surface broadcast; BCI: broadcast incorporated; SB: surface band; BI: band incorporation.



\* only one comparison for NUE in this subgroup.

**Fig. 8.** Impacts of soil tillage methods on the effects of EENF on area- and yield-scaled  $N_2O$  emissions, crop yield and NUE. The abbreviations in this figure were: CT: conventional tillage; RT: reduced tillage; NT: no-tillage.

#### 4. Study limitations

The EENF has many products, such as DCD (nitrification inhibitor), NBPT (urease inhibitor) and PCF (slow release fertilizer). Their pathway controlling the N releasing and transformation were different from each other. Some previous studies (Abalos et al., 2014; Gilsanz et al., 2016; Yang et al., 2016) have evaluated the efficacy of DCD and DMPP on crop yield or  $N_2O$  emission under specific soil or management conditions. Besides nitrification inhibitors, this study synthetically analyzed the impact of climate, soil and agronomic factors on the efficacy of S/CRF. However, the evaluation on UI is still limited. Though, in general, the efficacy of UI on  $N_2O$  emission and crop yield did not showed significant difference compared with other EENF products (Fig. A2); its effect size showed wide variation. Thus, more work is needed to investigate the effectiveness of UI under specific condition, which may be different from other EENF products.

The N form may affect the efficacy of EEN. Yang et al. (2016) has reported that DMPP was effective on the mitigation of  $N_2O$  emission along with organic fertilizer and ammonium sulphate nitrate, but not effective along with urea. In this study, we did not differentiate the impact of N form on the effects of EENF, as most of the N source was urea in the selected studies. Additionally, the response of  $N_2O$  emission to EENF was possibly influenced by the N application rates. The results of this analysis showed both IS and S/CRF were positive to the mitigation of yield-scaled  $N_2O$  emission from maize field only under low or high N rates. However, it was still unclear the performance of IS and S/CRF in wheat field under medium N rates due to the limited comparisons for wheat. Besides N application rates, examining the relationship of other indexes of N rates (such as excess N rate) with the efficacy of EENF may provide more practical information. However, most of the selected studies only investigated the efficacy of EENF under one or two N rates. It was hardly to analyze the other indexes of N rates in this analysis.

The releasing and transformation of N from EENF was different from conventional N fertilizer. So, the agronomic practice may be adjusted for EENF to obtain the best production and environmental benefits. However, the best management practice for EENF has not been well documented. This study only examined the impacts of N application timing, placement and tillage on the efficacy of EENF. More agronomic practices, such as irrigation, straw mulching, or planting methods, were needed to be investigated. Furthermore, it was potentially that the effective of EENF was affected by the interaction of different agronomic practices (e.g. tillage interacted with placement methods) or climate with agronomic factors (Halvorson et al., 2014). Further analysis is needed to evaluate the interaction of these factors on the effectiveness of EENF, which would provide more precise reference for the application of EENF in crop production. Integrated data analysis needs large datasets of field experiments. More field experiments are needed to be encouraged to investigate the best agronomic practices for EENF in future.

#### 5. Conclusion

This meta-analysis formulated two major generalizations regarding the effects of EENF on  $N_2O$  emission and crop yield. First, IS showed significant effects on the mitigation of  $N_2O$  emission and enhancement of crop yield; while S/CRF only significantly reduced  $N_2O$  emission, its effect on crop yield was not significant. In general, S/CRF was less effective than IS on the mitigation of yield-scaled  $N_2O$  emission. Second, the effects of IS and S/CRF were highly dependent on climate, soil properties, and agronomic practices. IS showed relatively greater effects on yield-scaled  $N_2O$  emissions in arid regions, in alkaline or fine soils, under reduced tillage, and when N applied rates  $> 180 \text{ kg ha}^{-1}$ . On the other hand, it did not show significant effects on the yield-scaled  $N_2O$  emission when fertilizer was surface broadcast and at N



application rates between 120 and 180 kg ha<sup>-1</sup>. The efficacy of S/CRF depended more on these factors. Humid climate, acid and coarse soils, medium N rate, SBC, and BI were not conducive for S/CRF to mitigate the yield-scaled N<sub>2</sub>O emission. Agronomic practices and climate factors possibly had interaction impact on the efficacy of IS and S/CRF. These results are useful guidance in the application of EENF for mitigating N<sub>2</sub>O emission without crop yield reduction.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.agee.2016.06.038>.

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